SUPPLEMENTARY INFORMATION

Understanding the molecular basis for the controlled design of ruthenium nanoparticles in microporous aluminophosphates

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**AIPO substitution mechanisms**

**Scheme S1:** Detailing the isomorphous metal-substitution mechanisms available in AIPO materials. The Al(III) and P(V) T-atom tetrahedral in the AIPO framework can be replaced with a range of transition-metals, creating isolated active sites.

**In-depth structural and textural characterisation**

**Figure S1:** Powder XRD patterns of the AIPO-5 and undoped RuAIPO-5 systems, both showing phase pure AFI.
Table S1: ICP, textural and unit-cell parameters for ruthenium-doped AlPO-5 (RuAlPO-5) and undoped AlPO-5.

<table>
<thead>
<tr>
<th></th>
<th>Metal Analysis</th>
<th>BET</th>
<th>P6cc unit cell parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al/wt%</td>
<td>P/wt%</td>
<td>Ru/wt%</td>
</tr>
<tr>
<td>RuAlPO-5-O-400</td>
<td>16.5</td>
<td>20.7</td>
<td>2.90</td>
</tr>
<tr>
<td>AIPO-5</td>
<td>16.7</td>
<td>18.1</td>
<td>-</td>
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Complementary EXAFS and Mass spectrometry data

Figure S2: The derivative of $\mu(E)$ for standard compounds and RuAlPO-5-AS, confirming the intermediary characteristics of RuAlPO-5-AS between Ru(IV)O₂ and Ru(III)Cl₃.xH₂O.
**Figure S3:** The variations in the magnitude of the $k^2$ weighted Fourier transform, contrasting the as-synthesised material with one heated to 179 °C under oxidative conditions.

**Figure S4:** Mass-spec data detailing the evolution of gases between specific scans in the RuAlPO-5-O series, showing the evolution of hydrogen gas.
Figure S5: The variations in the magnitude of the $k^2$ weighted Fourier transform, examining the effect of oxidative calcination on ruthenium with temperature, focusing on the metallic-phase transformations (189 °C).

Figure S6: Variations in the magnitude of the $k^2$ weighted Fourier transform, examining the effect of oxidative calcination on ruthenium with temperature, focusing on the metallic-phase transformations (189 °C), contrasting with known standards.
Figure S7: Changes in the magnitude of the $k^2$ weighted Fourier transform, probing the effect of oxidative annealing on ruthenium with temperature and contrasting the as-synthesised oxidic environment with that obtained under more extreme annealing conditions.

Figure S8: Variations in the magnitude of the $k^2$ weighted Fourier transform, examining the effect of inert annealing on ruthenium with temperature and contrasting the as-synthesised oxidic environment with that obtained under more extreme annealing conditions.
Figure S9: TEM images of the RuAIPO-5-O series at increasing temperature showing small nanoparticles (< 3 nm) in all cases. Increases in temperature lead to significant nanoparticle agglomeration.

Figure S10: Energy dispersive X-ray spectroscopy images highlighting the elemental distribution of RuAIPO-5-O-200. The figures show ruthenium is present in areas where the oxygen, aluminium and phosphorus signals are weakest suggesting metallic ruthenium.
**Figure S11**: Energy dispersive X-ray spectroscopy images highlighting the elemental distribution of RuAlPO-5-O-300. The figures show ruthenium is present in areas where the oxygen, aluminium and phosphorus signals are weaker suggesting metallic ruthenium with some oxidic content.

**Figure S12**: Energy dispersive X-ray spectroscopy images highlighting the elemental distribution of RuAlPO-5-O-400. The figures show oxygen intensity is invariant of ruthenium distribution, suggesting ruthenium oxide has been formed.
**Figure S13**: TEM images of the RuAlPO-5-I series at increasing temperature showing small nanoparticles (< 3 nm) in all cases. Increases in temperature lead to significant nanoparticle agglomeration.

**Further catalytic data**

**Figure S14**: Comparing the effect of annealing temperature under air atmosphere on the peroxide efficiency of RuAlPO-5 for the oxidation of cyclohexane. Conditions: 13 mmol cyclohexane, 13 mmol TBHP (70 wt% in H₂O), 0.05 g of RuAlPO-5 and 5 ml of acetone, 70 °C, 6 hours.
Figure S15: Comparing the effect of annealing temperature under nitrogen atmosphere on the peroxide efficiency of RuAlPO-5 for the oxidation of cyclohexane. Conditions: 13 mmol cyclohexane, 13 mmol TBHP (70 wt% in H$_2$O), 0.05 g of RuAlPO-5 and 5 ml of acetone, 70 °C, 6 hours.

Figure S16: Comparing the effect of annealing temperature under nitrogen atmosphere on the conversion and selectivity profiles of RuAlPO-5 for the oxidation of cyclohexane. Conditions: 13 mmol cyclohexane, 13 mmol TBHP (70 wt% in H$_2$O), 0.05 g of RuAlPO-5 and 5 ml of acetone, 70 °C, 6 hours.
Figure S17: Comparing the selectivity of different ruthenium containing systems for the oxidation of cyclohexane. Conditions: 13 mmol cyclohexane, 13 mmol TBHP (70 wt% in H₂O), 0.05 g of RuAlPO-5 and 5 ml of acetone, 70 °C, 6 hours.

Repeatability

Table S2: Detailing reproducibility between experiments and different batches of catalysts. All units are in mol%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conversion</th>
<th>Yield(Cyol)</th>
<th>Yield(Cyone)</th>
<th>Yield(Diol)</th>
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<tbody>
<tr>
<td>RuAlPO-5-I-400</td>
<td>17.7</td>
<td>2.6</td>
<td>6.5</td>
<td>8.7</td>
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<tr>
<td>RuAlPO-5-I-400</td>
<td>15.1</td>
<td>4.2</td>
<td>6.2</td>
<td>4.5</td>
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<tr>
<td>Repeat Reaction a</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RuAlPO-5-O-200</td>
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<td>4.2</td>
<td>6.6</td>
<td>9.9</td>
</tr>
<tr>
<td>RuAlPO-5-O-200</td>
<td>18.1</td>
<td>5.1</td>
<td>4.1</td>
<td>9.0</td>
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<tr>
<td>Separate Batch b</td>
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</table>

Conditions: 13 mmol cyclohexane, 13 mmol TBHP (70 wt% in H₂O), 0.05 g of RuAlPO-5 and 5 ml of acetone, 70 °C, 6 hours.

a) This reaction was performed with the same batch of catalyst that the characterisation and catalysis was performed on. The error in conversion is within 3%, the threshold for GC analysis.

b) This reaction was performed on a separate batch of catalyst to show the reproducibility of this method. Note errors are all within 2.6 mol%, lower than that of the threshold for GC error.